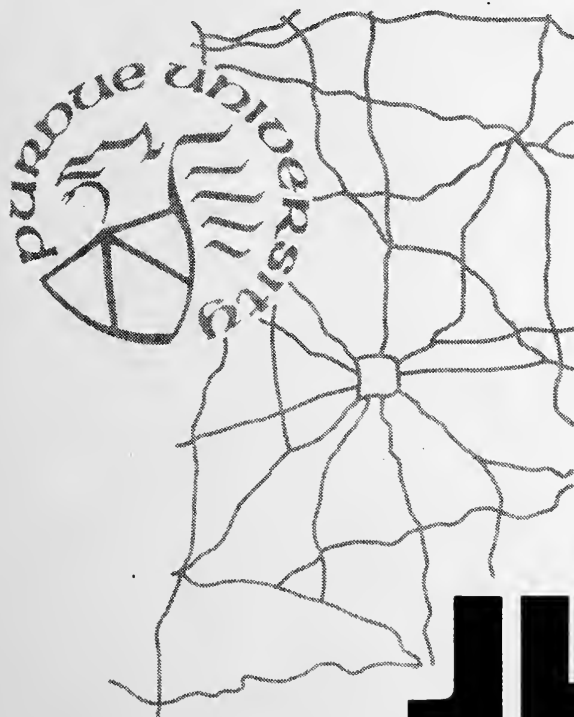# A MERCURY POROSIMETRY STUDY OF THE EVOLUTION OF POROSITY IN PORTLAND CEMENT

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BY

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AND
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JHRP

JOINT HIGHWAY RESEARCH PROJECT
PURDUE UNIVERSITY AND
INDIANA STATE HIGHWAY COMMISSION

A Mercury Porosimetry Study of the Evolution of Porosity in Portland Cement

To: J. F. McLaughlin, Director   4 November 1969
       Joint Highway Research Project

From: H. L. Michael, Associate Director   Project: C-36-61E
      Joint Highway Research Project
                                           File: 5-14-5

        The attached technical paper, "A Mercury Porosimetry Study of the
Evolution of Porosity in Portland Cement" by D. N. Winslow and S. Diamond
is derived from the Final Report on Phase I of the HPR Part II research
project "Fundamental Studies in Portland Cement Concrete".

        The paper reviews the mercury intrusion technique for measurement of
pore size distribution in porous media, presents experimental results on
such measurements in hydrated portland cement paste of various ages, and
interprets the results in the form of a consistent picture of the develop-
ment of microstructure as cement paste hydrates over a period of time.

        The paper has been presented orally at the July 1969 meeting of the
ASTM by Prof. Diamond. It is now presented to the Board for approval and
for transmission to BPR and ISHC for review and approval for publication.
It is proposed for publication by ASTM in the Journal of Materials.

                                Respectfully submitted,

                                Harold Michael/WD

                                Harold L. Michael
                                Associate Director

HLM:pm
  cc: JHRP Board

Technical Publication

A Mercury Porosimetry Study of the Evolution
of Porosity in Portland Cement

by
D. N. Winslow
and
S. Diamond

Joint Highway Research Project

Project: C-36-61E
File: 5-14-5

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ABSTRACT

The pore-size distribution of two hydration series of cement pastes prepared at water:cement ratios of 0.4 and 0.6 was determined as a function of age using mercury porosimetry. The contact angle of mercury on thoroughly dried paste was measured as 117°; for "p"-dried paste it was found to be 130°. It was found that much of the pore space present at all ages occurred in pores between 0.1 μ and 0.01 μ; that is, in between the conventional notions of "capillary" and "gel" pore diameters. It was further observed that pore volume left unintruded by mercury at 15,000 psi was significantly less than the 28 percent by volume that should be present in mature pastes according to current notions of the nature of cement gel. On the basis of these observations and direct examination of fracture surfaces of cement paste it was concluded that most of the space present is neither conventional "capillary" nor conventional "gel" space but merely space between fine individual particles of cement hydration products.

Key Words

INTRODUCTION

Notions of the microstructure of portland cement paste derived
mostly from the postulations of T. C. Powers and co-workers as ex-
tended by various workers are coming increasingly into question as
data based on new investigative techniques are reported. One of
the most fundamental of these notions is that in hydrating cement
paste two distinct kinds of pores were presumed to be present:
"capillary" pores which represent remnants of intergranular space
left unfilled by the various products of cement hydration (lime,
calcium silicate hydrate gel, hydrated calcium sulfoaluminates,
etc.), and "gel" pores. The latter were presumed to be a char-
acteristic feature inherent in the nature of hydrated cement paste,
occupying approximately 28 percent of its volume, and according
to Powers' 1960 estimate (1), having a width of the order of 18 A.
Powers also suggests in the same review paper that capillary pores
are "generally orders of magnitude larger than gel pores, even
in mature paste.

Direct examination of cement paste by scanning electron micro-
scopy (2,3,4) suggests that cement paste is, in fact, largely a
particulate system composed of primary particles of various
shapes and sizes, but with characteristic dimensions of the order
of 0.1 micron to a few microns. Examination of fracture surfaces
at high magnification also discloses that spaces ('pores') of
the order of a small fraction of a micron are present between the

primary particles of cement hydration products. Figure 1 shows a typical example. In addition, often a portion of the hydrated paste is seen to consist of reticular, spongy areas with visible holes or discontinuities of the order of 0.1 micron or less in diameter. An example of this is shown in Figure 2.

In consequence of these observations, it would seem that a more realistic idea of the pore structure of hydrated cement paste needs to include recognition of such pores intermediate in size between conventional notions of capillary and gel pores. Further, if a significant content of such intermediate pores occurs in mature paste, the volume of gel pores present might be less than the 28 percent conventionally estimated, perhaps significantly less.

The present work represents an attempt to explore and evaluate the content of pores of various size ranges in a series of portland cement pastes of increasing age prepared from a single cement. The focus of the problem is to secure a valid pore-size distribution curve, not only for a given paste, but for pastes representing the whole process of cement hydration. In this way some notion of the origin and changes undergone by the microstructural features of the paste might be developed.

The method chosen was that of mercury porosimetry. This procedure, while suffering from certain arbitrary assumptions that will be discussed later, represents the most nearly direct assay of pore sizes available at the present time. Alternate techniques, such as those involving capillary condensation, involve assumptions

that in fact are quite difficult to fulfil in cement paste studies.

HYDRATION OF CEMENT PASTE

The cement used throughout was a commercial Type I cement of Blaine fineness of 3380 cm^2/g with a composition of 51 percent C_3S, 24 percent C_2S, 11 percent C_3A and 6 percent C_4AF calculated according to the Bogue method. Analysis disclosed a gypsum content of 4.1 percent as $CaSO_4$, a free lime content of 0.72 percent and a total alkali content of 0.38 percent as Na_2O.

All mixing and curing operations were carried out at room temperature, approximately $24^{\circ}C$, in an air-conditioned laboratory.

Mixing was done in vacuo in a specially made cylindrical plastic mixer, which was loaded with several steel rods and flint balls and a standard charge of 1000 g of cement, and then evacuated. Water was added through a valve without breaking the vacuum, and the mixer then alternately rolled on an electric roller at 100 rpm and shaken by hand, according to a preset schedule for a total of 25 minutes. The vacuum was then released and the paste placed into 12-ml polypropylene test tubes by rodding in three layers on a vibrating table. A tight fitting stopper was then positioned so that no free volume was left above the paste and vibration continued with frequent reversal of top and bottom according to a preset schedule. The samples were then stored (stoppered) in a fog room for 24 hours, demolded directly into saturated limewater, and allowed to hydrate continuously until the desired age was attained.

Checks of density confirmed essentially complete uniformity within each cylinder except for the top and bottom ends; in practice, specimens for analysis were taken only from the middle one third of each cylinder and the outer two thirds discarded.

Two series of pastes were made, one at a water:cement ratio or 0.6, the other at 0.4. Approximately 320 individual cylinders were prepared for this work, and pore-size distributions were run on approximately 80 of them.

Considerable preliminary work was done to determine the most appropriate drying technique, since it is necessary to begin a mercury porosimeter run with all of the sample pores vacant. As the result of a number of comparisons of the results of various standard methods of drying ("P-drying" over a mixture of magnesium perchlorate hydrates, "D-drying" over a dry ice trap, and oven drying at 105°C) the oven-drying procedure was selected as the standard procedure. A discussion of these experimental comparisons is given subsequently in this paper. All samples tested for pore-size distribution were oven dried, broken into pieces of the order of one gram in weight, and then tested in the bulk condition, i.e, not ground to a powder.

DETAILS OF THE DETERMINATION OF PORE-SIZE DISTRIBUTION BY MERCURY POROSIMETRY

Theory

A non-wetting liquid (i.e. one forming a contact angle with a given solid greater than 90°) will intrude open pores of the

solid only under applied pressure. The pressure required is a
function of the contact angle, the surface energy of the liquid,
and the geometry of the pores. For the case of cylindrical pores
the relation given by Washburn (5) is:

$$P = \frac{-4\ \gamma\ \cos\ \theta}{d} \qquad (1)$$

where: P = pressure required to intrude pore

         d = diameter of intruded pore

         γ = surface energy of the liquid

         θ = contact angle between liquid and pore wall

Mercury is almost always used as the liquid as it has a number
of practical advantages including low vapor pressure, relative inert-
ness in terms of chemical reactivity, and the fact that it is nor-
mally non-wetting for most kinds of surfaces.

The practical upper limit of pore diameters measurable by
mercury porosimetry may be extended to about 1000 microns or more
by appropriate techniques; the lower limit is usually set by the
pressuring capacity of the instrument although considerable uncer-
tainty accompanies the use of very high pressures corresponding to
pores of only a few molecular diameters. In the present work the
upper limit of measurement was taken to 200 microns, although for
most pastes very little pore space was found for diameters larger
than 10 microns. The lower diameter limit was set by the pressuring
capacity of the instrument used, approximately 15,000 psi, and
corresponds to about 82 A (0.0032 microns) for oven dried paste.

There are certain limitations inherent in the mercury pore-size distribution technique. At the outset of a mercury intrusion determination the sample is surrounded by mercury; as pressuring procedes, mercury flows from the surface of the sample towards its center through whatever pores are available to it. If the path mercury must follow to reach a particular internal pore is smaller in diameter than the internal pore itself, that pore will be intruded only after sufficient pressure is applied to intrude the narrower pathway. Thus, fundamentally, pores accessible only through restricted entryways are tallied as part of the diameter class of the entryways. Since entryways narrower than 82 A could not be intruded in this work due to the pressure limitation, pores of any size connected to the exterior only by entryways narrower than 82 A will not have been measured. Finally, isolated pores having no communication with the exterior of the sample cannot be measured in any event, regardless of the pressure used.

Apparatus

The instrument used to measure mercury intrusion was an American Instrument Co. unit (Catalogue No. 5-7121) with an operating pressure maximum of 15,000 psi, modified in certain respects. The porosimeter consists essentially of a means of generating pressure to cause intrusion and a means of measuring the volume of mercury intruded. We found that the electric motor which drove the pressure generator caused the porosimeter to heat up during use, thus affecting the measurement of the intruded mercury. To avoid this we removed the back of the

instrument cabinet and relocated the electric motor some distance away. The portion of the equipment used to measure coarse pores (the "filling device") was discarded and replaced by a unit of advanced design (U. S. Patent No. 3,438,245, Prado Laboratory, Inc., Cleveland, Ohio). With the modified unit, the filling device and sample holder (a dilatometer-like vessel called a penetrometer) are maintained in a horizontal position during all filling and measurement operations, thus permitting operation substantially free of any pressure applied by the weight of superposed mercury, and extending the upper limit of the range of diameters measurable from about 100 microns to about 1000 microns.

Corrections For Intrusion Data

The basic data recorded in mercury porosimetry consist of a series of measurements of increasing absolute pressures on the mercury and corresponding cumulative volumes of mercury intruded. The apparent volume of intruded mercury that is read at each pressure step must be corrected for several different effects:

1) The residual air remaining in the penetrometer after evacuation is trapped during the initial mercury filling step, and is compressed progressively to increasingly small volumes as pressure increases. The change in volume due to compression of air must be subtracted from the gross intruded volume of mercury at each step. Since initial pressure and volume are known, Boyle's Law can be used to calculate the required corrections, which in the present work total about 0.001 cm^3.

2) The mercury is being consumed at the photocell. The required correction as measured from the change in volume of the liquid as indicated by the ...

Measurement of Contact Angle

In the absence in the available literature of any systematic contact angle measurements on mercury on quartz plates, ...

of measurements were carried out to determine this quantity. The
technique chosen was one which provides the most directly appli-
cable measurement for the purpose in hand, and consists of a
direct measurement of the pressure required to intrude cylindrical
pores of an accurately known diameter. With the diameter and pressure
known, the factor $4 \gamma \cos \theta$ is calculated directly from Equation 1,
and assuming the well-established value for γ, (6,7) of 484 dynes/cm,
θ follows immediately. In point of fact, it is not strictly necessary
to calculate θ itself, since the factor $4 \gamma \cos \theta$ required for inter-
preting the mercury intrusion data is directly available from the
experimental measurement.

The measurements were performed on a 267-day old cement paste
of the 0.4 water:cement ratio series. A disk of paste about the
size and shape of a dime was cut from the cement paste cylinder
using a precision lathe and saturated limewater as the only lubri-
cant, and a series of 40 holes were drilled through the disk using
a No. 92 twist drill, again with limewater as the lubricant. Both
surfaces of the disk were examined under an optical microscope to
confirm the circularity of the cross-sections of the drilled
cylindrical pores and individual measurements of the diameter
of each pore were made. The average diameter was 201.5 microns;
most of the diameter measurements fell between 190 and 210
microns. The disk was then carefully "P-dried" over the appropriate
mixture of magnesium perchlorate hydrates (8), and then subjected
to mercury intrusion, the pressuring being carried only slightly
beyond that necessary to intrude the drilled pores. The mercury

spontaneously flowed out of the pores on reducing the pressure, so
that repeated measurements could be made. These were found to be
quite reproducible. Subsequently, the same sample was oven dried
at 105°C and the intrusion measurements repeated in the oven-dried
condition. The pressure and intrusion data are given in Figure 3.

The measurements indicate a contact angle of 130° for the "P-
dried" paste, but a contact angle of only 117° for the oven-dried
paste. The relationship between pressure and pore diameter (Equa-
tion 1) involves the cosine of the contact angle; thus, the 13°
difference in contact angle corresponds to a 30 percent drop in the
value of the cosine, and hence, in the diameter intruded at a given
pressure.

It is generally considered that "P-dried" pastes do, in fact,
contain some residual surface water, and the reduction in contact
angle on more complete dehydration of the surface on oven drying is
in line with similar changes reported on glass and other substances
(9). Thus, the value of 117° has been used in calculating pore
diameters for all of the cement pastes discussed in this paper,
all of which were oven dried prior to mercury intrusion.

Effects of Sample Drying

In preliminary studies, companion samples of cement pastes
were dried by each of the three drying procedures in common use
for cement paste: equilibration over magnesium perchlorates ("P-
drying"), evacuation over a dry-ice trap ("D-drying") (10), and
oven drying at 105°C. The methods are given in order of increasing
severity of water removal, the equilibrium vapor pressures being

8 μHg (11), and 0.5 μHg, respectively, for the first two methods.
The pressuring curves for the companion samples had similar shapes.
Use of the measured contact angles for "P"- and oven-dried samples
to interpret the data resulted in pore-size distribution curves
like those of Figure 4, in which it is seen that the data in the
coarse pore region roughly coincide, but that the extent of pore
space in diameter classes smaller than about 1000 A seems to be a
direct function of the rigor of the drying treatment. Data for
the "D-dried" condition fall in between the plots for the "P-dried"
and the oven-dried pastes, and are more nearly like the former. An
assumed contact angle of 126° was used in the absence of a measured
value for this drying condition. Nevertheless, it is quite clear
that the very small differences in residual water retained at
equilibrium with respect to the different drying treatments are
in some way responsible not only for the changed contact angle
but also the relatively large change in apparent mercury pore-size
distribution in the fine-pore region. That this phenomenon is not
associated with microcracking or other irreversible changes accom-
panying the more rigorous drying procedures is shown by the experi-
mental fact that the change is reversible. If a sample is dried
to weight equilibrium by any of the three techniques, resaturated,
and then redried by another technique, it will exhibit essentially
the same pore-size distribution to mercury as if it had originally
been dried by the second technique. Data illustrating this obser-
vation are given in Figure 5. Observation of these pastes by
scanning electron microscopy did not disclose any evidence for

microcracking in the size range concerned, thus confirming that differential microcracking associated with differences in drying procedure is not the cause of the differing pore-size distributions

As mentioned earlier, oven drying was finally selected as the standard technique for characterising the pore-size distribution of the pastes, largely on the assumption that the complete removal of water prior to the intrusion of mercury possibly provides a truer assessment of the actual pore system structure

Possible Influence of Carbonation

Some of the specimens to be tested [...]

[several heavily faded lines]

[...] exposure to the atmosphere, and it was concluded that exposure to the atmosphere did not influence the pore-size distributions obtained in this work

RESULTS

Presentation of Data

The experimental pore-size distribution data in this work are presented in the form of cumulative pore-size distribution curves

the pore volume parameter being expressed as cm^3 of pore space per
oven-dry gram of cement paste. The volumes are accumulated from
the largest diameter pore measured to the smallest, the order in
which the pores are physically intruded by the mercury. To retain
the normal sense of the logarithmic scale of the abscissa, the cumu-
lation curve procedes from lower right to upper left.

In presenting pore-size distribution data for limited ranges of
pore sizes many authors, particularly those who report results from
capillary condensation measurements, prefer to plot the derivative
distribution function, d (volume)/d (diameter), rather than the
cumulative or integral volume function. Unfortunately, the deri-
vative presentation is severely distorted for data covering several
orders of magnitude and vastly overemphasizes the apparent impor-
tance of the finest pore sizes at the expense of the coarser sizes.
Further, the integral function used here has the distinct advantage
that the fraction of pore space between any arbitrary bounds of
pore diameters can be assessed at a glance.

Pore measurements were originally made starting from a diameter
of several hundred microns, but it became apparent that even the
youngest pastes tested showed negligible intrusion for diameters
greater than 10 microns; the figures thus begin at that diameter.
The minimum pore diameter intruded was approximately 82 A.

In general, two replicate tests were conducted on a particular
paste, and in some cases three or four, Repeatability was excellent,
as seen in the figures presented.

Degree of Hydration, Total Pore Volume, and Pore Volume Intruded

Table 1 presents a summary of the samples employed, in terms
of water:cement ratio and age at testing. Tests were conducted

on 0.4 and 0.6 water:cement ratio pastes hydrated continuously
for periods ranging from one day to approximately eleven months.

The percentage of hydration recorded in Table 1 was obtained
simply as the ratio of the non-evaporable water (after oven drying)
of each paste at the stage concerned to that of a fully hydrated
product of the same cement hydrated for many months in a ball mill.

The total pore volume present in each paste at the stage con-
cerned was calculated in the following manner: First, the bouyant
weight (in water) of each paste in the saturated condition was
determined immediately on achievement of the required age; the
paste specimen was then oven dried, weighed, and the density of
solid matter calculated. The volume of solids was then calculated
from the weight and the density. The bulk volume of the oven-
dried sample was then determined by displacement of mercury, and
the difference between bulk volume and solid volume was taken as
the total pore space present and this was assessed as volume per
dry gram of the paste. This procedure assumes that the density
of water within the pores of the initially saturated specimen is
the same as that of ordinary water. If, as has been suggested on
the basis of indirect experiments (11), part of the water
that is in the finest pores or most closely associated with the
surface has a higher density, the density of solid matter will
be correspondingly overestimated, and the pore space figure will
be too low. The values calculated for the pastes are, in fact,
quite reasonable and one would not expect this to be a major effect.

Table 1 also contains, for each paste, the total volume of
mercury intruded into each sample. This is in all cases less than

the calculated volume of pore space. This is not surprising since pores having nominal diameters smaller than 82 A and pores penetrable only through necks smaller than 82 A cannot be recorded by the instrumentation employed. What is significant is that even for quite mature 0.4 water:cement ratio pastes, half or more of the pore space can in fact be intruded, i.e. consists of pores with nominal diameters significantly larger than the size range commonly associated with gel pores. This point will be discussed subsequently and its implications assessed.

Finally, the pore space calculated to be present, but not intruded by mercury up to the pressuring limitation corresponding to 82 A diameter is re-expressed as a percentage of the bulk volume occupied by the system. This percentage constitutes essentially an upper-bound estimate of the volume fraction of the finest class of pores present, i.e. those pores that would be assessed as "gel" pores on the basis of the prevailing model. It is an upper-bound estimate because it includes the volume of pores with diameters greater than 82 A but available to mercury only through constrictions smaller than this, and also any pores that happen to be completely isolated. According to the estimates of Powers (12), a fully hydrated paste of water:cement ratio larger than that required to provide room for complete hydration (i.e. larger than 0.38) should have a content of gel pores of 28 percent by volume. The figures in the last column of Table 1 reveal that for the oldest of the pastes tested (which are 80 percent and 86 percent hydrated, according to our estimates) there is an upper bound estimate of about 18 percent by volume in pores not intruded by mercury, i.e.

seemingly finer than 82 A in diameter. This upper bound estimate is much less than the volume of gel pores that would be present according to Powers. Furthermore, the data do not suggest that further increments of hydration associated with increasing age would lead to any major increase in the experimental value.

Characteristics of the Distribution Curves

Figure 6 presents the cumulative pore-size distribution curves for the series of 0.6 water:cement ratio pastes hydrated for periods of 1,2,3,5,7,28,59, and 318 days, respectively. A similar set of results is presented in Figure 7 for the corresponding 0.4 water: cement ratio pastes.

The following observations may be made on examining the general form and appearance of the curves:

1. The general distribution shifts to the left with increasing age; that is, the pores become increasingly finer with age.

2. The total pore volume intruded decreases with increasing age.

3. All of the curves display an apparent "threshold diameter", above which there is comparatively little intrusion into the paste, and immediately below which the greatest portion of the intrusion commences. The threshold diameter decreases steadily with age.

4. At any given age both the total intruded pore space and the threshold diameter are significantly larger for the 0.6 water:cement ratio paste than for the corresponding 0.4 water:cement ratio paste.

5. To a surprising degree the overall shapes of the distribution curves as plotted on a logarithmic diameter scale

are similar to each other. The only significant exception
to this statement is the fact that the mature (28 days or
older) 0.6 pastes show cumulative distribution curves that
are approximately linear with the log of the diameter, while
the corresponding curves for the 0.4 pastes tend to flatten
out below about 300 A.

These general observations are now discussed in detail.

Decrease in Overall Pore Size with Age

This general observation is entirely in accord with ordinary
expectation, based either on the Powers model or the simple obser-
vation that the hydration products of cement are, in general, signi-
ficantly finer in particle size than the original cement grains.
In consequence, one expects that the residual spaces present de-
crease as the content of hydration products increases with increasing
age.

Figure 8 documents this trend quantitatively, by plotting the
volume-average pore diameter as a function of age for each of the
two water:cement ratio series. For almost all of the pastes the
intrusion measured was greater than half the total pore space; thus,
the volume-average pore diameter can be calculated without knowledge
of the distribution of remaining fine pore sizes not tallied. In
each case the diameter cited is an underestimate to the extent that
"ink bottle" pores influence the observed distribution. The aver-
age diameters for day-old pastes, about 3000 and 1200 A respect-
ively for the 0.6 and 0.4 pastes, drop rapidly to less than 300 A
by a week of hydration; then drop much more slowly to values of the
order of 100 A.

Decrease of Intruded Pore Volume with Age

Again, such a result should be expected both on the basis
of the Powers model of hydration and on the general notion that
the hydration products occupy more volume than that occupied by
the cement grains they replace. Quantitatively, as seen from
Table 1, intrusion drops from about 0.36 cm^3/g for 1 day old paste
to about 0.19 cm^3/g for 318 day old paste of 0.6 water:cement
ratio; the corresponding figures for the 0.4 pastes are 0.27 and
0.10 cm^3/g, respectively.

Threshold Diameter and Its Significance

The decrease of the previously defined "threshold diameter",
with age is documented in Figure 9. The pattern of decrease is
somewhat similar to that for mean diameter as a function of age
(Figure 8) but naturally the threshold diameters are much larger
for a given age. Beyond seven days the threshold diameter, like the
volume-average diameter, ceases to decrease very rapidly.

The significance to be attributed to the threshold diameter
is not immediately apparent, and some additional experiment was
helpful in its interpretation. Samples of paste were pressured
to pressures just less than, and also slightly greater than, the
pressure corresponding to the threshold diameter. The samples
were then depressurized, broken open, and fracture surfaces examined
in an optical microscope. The total intrusion that had taken
place was slight, in either case, compared to the total intrusion
possible for the sample at high pressures. Nevertheless, signi-
ficant differences were noted in the color and in the appearance

of the samples under the microscope. The color of the sample
intruded to less than the threshold diameter was light gray;
microscopic examination disclosed localized "streams" of mercury
along the fractured cross-section of the interior, but also many
local regions were present within the microscope field with little
observable evidence of penetration by mercury. In contrast, the
sample pressured to just beyond the threshold value was dark gray
in color; examination under the optical microscope revealed the
presence of darkened areas and droplets of exuding mercury uniformly
spaced over all regions of the fracture surface. Macrophotographs of
an unintruded paste specimen and specimens intruded to just below and
just above the threshold diameter are given in Figure 10.

Additional information bearing on the nature of the threshold
diameter had to do with the time required to reach equilibrium
in a given increment of intrusion of mercury. It was noted that
a drastic slowing down of the rate of penetration of mercury
seemed to take place while making intrusion measurements near
the threshold diameter. A series of special runs were made in
which the time to reach equilibrium was noted at each pressuring step.
Typical results of such determinations are given in Figure 11.
The data are plotted in terms of the equilibration time per unit
volume intruded, i.e. an inverse rate of penetration, vs. nominal
diameter. Data are given for 2 day old and 318 day old pastes
of both water:cement ratios. It is clear that at the threshold
diameter, the rate of penetration of mercury is exceedingly slow
compared to the rate both for intrusion into the coarser pores

and for intrusion into the bulk of the pore space in pores finer
than the threshold diameter.

These observations are interpreted in the following manner.
It is considered that the threshold diameter represents the minimum
diameter of pores which are geometrically continuous throughout
all regions of the hydrated cement paste. Some pores of diameter
larger than this are present and available to the exterior, especially
for the 0.6 pastes; but the volume of such easily available coarse
pores is small and they are easily intruded from the exterior of
the specimen. Pores larger than the threshold diameter, but
available to the outside only through the continuous pore system,
are likely also present to some extent. As the pressure corres-
ponding to this characteristic diameter is reached, mercury
begins to flow into new regions of the sample from the exterior
of the paste. This flow presumably follows a long, tortuous
path, and since essentially all of the mercury has to flow into
the paste from new locations at or near the exterior, the process
is correspondingly slow. Finally, perhaps at a pressure slightly
in excess of that corresponding to the initial slowing down, the
geometrically continuous channel system leading through all micro-
regions of the paste is filled. Further intrusion (and by far
the greater portion of the pore space has yet to be intruded)
comes about through a process of filling what must be local side-
channels and pores of finer and finer diameter from mercury already
in the continuous channels. This filling of secondary pores,
constituting the bulk of the pore system, is again rapid, since

flow paths are short. Thus the pore system of cement paste is visualized as constituting a geometrical system analagous in some respects to a finely branched river system with the relatively large pores intruded at the threshold diameter corresponding to the major rivers flowing through a geographical region, and the rest of the pores corresponding to local branch streams. The intrusion process corresponds, of course, not to drainage but to a hypothetical reverse flow from the river mouths.

The phenomenon of slow intrusion at a threshold diameter has been observed by N. M. Winslow of Prado Laboratories for a large number of other types of porous materials (private communication).

Influence of Water:Cement Ratio

As noted, and again in accord with all reasonable expectation, all of the parameters describing porosity are larger for the 0.6 water:cement ratio pastes than for the 0.4 water:cement ratio pastes of the same age.

What appears to be of some significance to the writers is the fact that the parameters, in general, are not so very much greater for the 0.6 as compared to the 0.4 pastes. For example, the threshold diameters of Figure 9, the volume-average pore diameters of Figure 8, and the general appearance and location of the cumulative curves of Figures 6 and 7, indicate that the pores of the 0.6 paste series are, as the pastes age, not really different in general size range than those of the 0.4 paste, especially after the first day. This is not at all in accord

with the notions of hydration formally encompassed in the
Powers model, on the basis of which one would envision that
the excess capillary space available at all stages for the 0.6
paste should remain in very large pores commensurate in size
with the original pores present at the time of set.

General Pattern of the Pore-Size Distribution Curves

The approximately similar shapes of the pore-size distri-
bution curves with aging do not lend support to the notion that
the hydration process consists of replacing large units of
capillary space with more or less single sized pores of a char-
acteristic and very fine diameter. Rather it appears to the
writers to be indicative of a general and continuing process
of subdivision of pores.

In this context, the evolution with time of the intermediate
size class of pores is instructive. For example, if one examines
the apparent content of pores between arbitrary boundaries of
0.1μ (1000 A) and 0.01μ (100 A), one finds a gradual increase
at first, then a gradual decrease as the general porosity becomes
finer. For the 0.6 series, the apparent content of pores between
these size boundaries is 0.080 cm^3/g at one day, increasing to about
0.175 cm^3/g at 28 days, and then decreasing slightly to about 0.160 cm^3/g.
Corresponding figures for the 0.4 series are 0.085 cm^3/g at one day,
increasing to about 0.150 cm^3/g at seven days, and then decreasing grad-
ually to about 0.100 cm^3/g. Thus, it may be argued that the reduction in
pore size with age is not accomplished by replacing large ("capillary")

pores with very fine ("gel") pores without regard to intermediate
sizes, as conventional formulations would imply, but rather one
of continuous narrowing of pores as particulate hydration products
are laid down. In such a process the content of intermediate-
sized pores would be expected to increase as the coarse pores
are initially subdivided, and then gradually decrease as spaces
between grains of hydration products grow finer and finer; this
is exactly what seems to happen.

CONCLUSIONS

1. Mercury intrusion of dried cement paste supplies a reproducible
    and apparently satisfactory direct method for the assessment
    of pore-size distributions, provided due caution is displayed
    in experimental details, in insuring completeness of water
    removal by rigorous drying, and in use of a realistic contact
    angle value. Due regard should be paid to the possible exis-
    tence of ink-bottle pores, isolated pores, and to the defficiency
    of the pore shape model.

2. Direct measurements confirm the general concept that as a paste
    hydrates the total pore volume decreases and a general reduction
    in pore sizes takes place.

3. The measurements are in contradiction to specific notions of
    the nature of cement paste generally accepted. The content of
    pores finer than 82 A as estimated by difference between in-
    truded volume and total volume is significantly less than the
    volume of "gel" pores assumed to be present on the basis of
    cement models. The content of pores between 0.1 μ and 0.01 μ,

"in-between" capillary and gel pore sizes by current notions, is found to be very substantial at all ages.

4. The evidence points toward a notion that most of the volume in cement paste is neither "capillary" porosity nor "gel" porosity per se, but largely consists of spaces left between particulate hydration products, perhaps supplemented by pores on apparently spongy hydration products occasionally found to be present in scanning electron microscope observation.

5. The existence of a "threshold diameter" for mercury intrusion in paste is noted; and its regular decrease with age documented. It is associated with very slow intrusion and with a qualitative difference in completeness of penetration of mercury to all general regions of the sample. It is concluded that the threshold diameter corresponds approximately to the minimum diameter of channels that are essentially continuous through the paste at a given age.

ACKNOWLEDGEMENTS

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Table I
Summary of Pore Volume Data

Water: Cement Ratio	Age (days)	Degree of Hydration (%)	Calculated Total Pore Volume (cm³/g)	Pore Volume Intruded		Pore Volume Not Intruded		% of Bulk Volume
				Volume (cm³/g)	% of Total Calculated Pore Volume	Volume (cm³/g)	% of Total Calculated Pore Volume	
0.4	1	38.0	0.323	0.266	82	0.057	18	8.6
0.4	2	45.7	0.298	0.231	77	0.067	23	10.4
0.4	3	52.9	0.279	0.194	70	0.085	30	13.3
0.4	5	59.5	0.265	0.182	69	0.083	31	13.2
0.4	7	62.8	0.260	0.175	67	0.085	33	13.6
0.4	28	72.4	0.231	0.151	65	0.080	35	13.3
0.4	60	75.3	0.218	0.109	50	0.109	50	18.4
0.4	320	80.1	0.209	0.100	48	0.109	52	18.6
0.6	1	39.6	0.412	0.360	87	0.052	13	6.9
0.6	2	50.2	0.391	0.327	84	0.064	16	8.6
0.6	3	53.2	0.373	0.300	80	0.073	20	10.0
0.6	5	61.5	0.365	0.272	75	0.093	25	12.8
0.6	7	65.4	0.360	0.249	69	0.111	31	15.5
0.6	28	76.5	0.337	0.226	67	0.111	33	16.0
0.6	59	80.7	0.323	0.204	63	0.119	37	17.3
0.6	318	86.4	0.306	0.187	61	0.119	39	17.5

Legends for Figures

Figure 1   Scanning electron micrograph of cement paste fracture
               surface, water:cement ratio 0.6, hydrated 7 days, showing
               sub-micron pore space.

Figure 2   Scanning electron micrograph of cement paste fracture
               surface, water:cement ratio 0.6, hydrated 7 days, showing
               reticular spongey area between lime crystals.

Figure 3   Mercury intrusion data for cement paste disk used for
               measurements of contact angle.

Figure 4   Influence of sample drying procedure on measured pore
               size distribution. Cement paste has water:cement ratio
               of 0.4, hydrated 158 days.

Figure 5   Pore size distribution measurements illustrating rever-
               sibility of drying effect. Cement paste has water:cement
               ratio of 0.4, hydrated 158 days.

Figure 6   Pore size distributions of water:cement ratio 0.6 cement
               pastes hydrated for various ages.

Figure 7   Pore size distributions of water:cement ratio 0.4 cement
               pastes hydrated for various ages.

Figure 8   Mean pore diameters as functions of age for two water:
               cement ratios.

Figure 9   "Threshold diameters" as functions of age for two water:
               cement ratios.

Figure 10   Fracture surfaces of cement paste. Top; unintruded.
               Center; intruded to diameter just larger than "threshold
               diameter". Bottom; intruded to diameter just smaller than
               "threshold diameter".

Figure 11   Inverse rate of mercury intrusion as a function of pore
               diameter for mature cement pastes.

Cumulative Intrusion ($ml \times 10^{-4}$) vs Pressure (mm. Hg)

⊙, ▫ "P" Dry Replicates

●, ■ Oven Dry Replicates

Cumulative Pore Volume (cm³/gm.) vs. Pore Diameter (μ)

Legend:
● Oven Dried Θ=116°
■ "P" Dried Θ=130°
○ Assumed "D" Dried with Θ=126°

Legend (within figure):
- ● Oven dried.
- ○ Oven dried after initial "P" drying and resaturation.
- △ Oven dried after initial Oven drying and resaturation.
- ■ "P" dried.
- □ "P" dried after initial Oven drying and resaturation.

Cumulative Pore Volume (cm³/gm)

Pore Diameter (μ)

Cumulative Pore Volume (cm³/gm) vs. Pore Diameter (μ) for curves labeled: 1 day, 2 days, 3 days, 5 days, 7 days, 28 days, 59 days, 318 days.

Age (days)

Mean Pore Diameter (μ)

□ w/c = 0.6
○ w/c = 0.4

The chart is a plot of Equilibrium Time per Unit Volume (min/cm³ x 10⁴) versus Pore Diameter (μ).

Legend:
- w/c = 0.6, age = 318 days
- w/c = 0.6, age = 2 days
- w/c = 0.4, age = 320 days
- w/c = 0.4, age = 2 days